Title	Thermodynamic Analysis of Ammonia-Water-Carbon Dioxide Mixtures For Designing New Power Generation Cycles.
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Abstract

Objectives

The goal of this project is to develop a computational package for the prediction of thermodynamic properties (vapor-liquid equilibrium, specific heat, volume, bubble and dew points, solubility, corrosivity) for ammonia-water-carbon dioxide mixtures at high temperatures and pressures. This package will be used for the design and analysis of hybrid power cycles. The specific tasks are:

1. Detailed literature review of existing thermodynamic property data and prediction methods for ammonia-water-carbon dioxide mixtures.
2. Development of detailed nonideal thermodynamic property prediction subroutines for these mixtures.
3. Use of the above models to fit and predict properties for the mixtures.
4. Development of simplified thermodynamic models, in smaller pressure-temperature ranges, for use in optimization based analysis and synthesis of advanced power cycles.

Accomplishments To Date

We have initiated our study with a review of thermodynamic data available on ammonia-water mixtures. Published thermodynamic property equations predict large deviations from experimental data at high pressure and temperatures (above the mixture critical point, which itself has not been measured accurately). Hence, we have first modified a set of empirical equations of state for the ammonia-water mixture developed by Ibrahim and Klein. We compared the predictions from this package with published experimental data, and the predictions agree very well for design purposes. Since there is a large set of nonlinear equations to be solved, the program is is not suitable for optimization where thousands of function evaluations may be required. To enhance the speed and robustness of this package, we have incorporated analytical gradients in the Newton based solver for the routine.

Next, we are trying to assess the feasibility of using this complicated model with optimization routines for the design and analysis of the power cycle. We have modified an earlier Kalina cycle optimization code to use this package. We employ both a deterministic optimizer, MINOS, and a stochastic one using differential evolution, a genetic technique. Our results show that for the optimal design to be achieved, a much simpler thermodynamic package is needed.

Therefore, we are developing a set of consistent linear estimators for the stream property states (compositions, temperature, pressure, enthalpy, entropy, etc.) that are estimated repeatedly as the cycle optimization proceeds. Each optimization iteration sees only a linear thermodynamic equation set. The validity of this fit is tested once the iteration converges, and this procedure is repeated to the solution.

Separately, we are also adding to the ammonia-water package the Wagner equation of state for carbon-dioxide mixtures. In the gas phase this will be adequate, whereas, in the liquid phase, we will account for ionic species and reactions through the equations proposed by Rumpf and Maurer. With this package, and the optimization technique above, we will be able to design and analyze the hybrid configurations for bottoming power cycle applications.

Significance To Fossil Energy Programs

Advanced power generation cycles, for *bottoming cycle* applications, have been proposed in the last decade that employ a mixture of *ammonia/water* and even *carbon-dioxide* instead of pure water as a working fluid in the cycle. *Efficiency improvements* of over 20% over conventional bottoming cycles are claimed for these cycles. Such power cycles will allow the efficient utilization of the nation's fossil reserves while reducing the emissions of greenhouse gases. Since these cycles are used in recovering heat from cogeneration turbines, they will form an integral part of DOE's Vision 21 advanced power coproduction facility.

Plans For The Coming Year

We plan to continue work on the development of adequate linear property equations to describe the ammonia-water-carbon dioxide mixture thermodynamics. We will evaluate these fits against rigorous thermodynamic equations, experimental data where available, and in terms of its suitability for use in design and optimization of power cycles.

Presentations and Student Support

Conference Presentations

We will be submitting two papers based on this work to the 1999 Annual Meeting of the American Institute of Chemical Engineers in Dallas in November. The PI is also organizing a session on "Separation System Design and Analysis" at this conference.

Students Supported Under This Grant

- Kumara Narasimha K Sastry, Graduate (Ph.D.) student in Chemical Engineering, University at Buffalo